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Original Citation:

Chemical Stripping of ceramic films of titanium aluminum nitride from hard metal substrates / U. Bardi; D. Bonacchi; G. Rizzi; A. Scrivani. - In: SURFACE & COATINGS TECHNOLOGY. - ISSN 0257-8972. - STAMPA. - 165:(2003), pp. 35-39. [10.1016/S0257-8972(02)00720-X]

Availability:

This version is available at: 2158/771782 since:

Published version:

DOI: 10.1016/S0257-8972(02)00720-X

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ELSEVIER

Surface and Coatings Technology 165 (2003) 35–39

**SURFACE
& COATINGS
TECHNOLOGY**

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Chemical stripping of ceramic films of titanium aluminum nitride from hard metal substrates

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Received 18 March 2002; accepted in revised form 19 September 2002

Abstract

We report here the result of a study of different chemical stripping methodologies for ceramic coatings deposited by PVD on hard metal substrates. We show that an approach based on the study of the system by surface science techniques leads to the possibility of developing effective stripping methods as well as guidelines for improving the process. We will report about two methods tested for the stripping of layers of titanium aluminum nitride (TINALOX) deposited by Physical Vapor Deposition (PVD) on hard metal substrates. The methods were based on (i) the combination of hydrogen peroxide and potassium oxalate in alkaline conditions, and (ii) potassium permanganate in a concentrated sulfuric acid solution. Of the two methods, the second (permanganate and sulfuric acid) appears to be the most promising, although further studies will be needed to optimize the process.

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Keywords: Photoelectron spectroscopy; X stripping; Magnetron; Titanium; Nitride

1. Introduction

Ceramic coatings deposited by physical vapor deposition (PVD) are becoming a fundamental element in the mechanical industry for improved hardness and corrosion resistance that they confer to treated parts. PVD processes can produce strong and compact thin films (most often in the micron range), generally nitrides and carbides. Titanium aluminum nitride, TiAlN₂ (under the commercial name of TINALOX) is a recently introduced material with excellent hardness and thermal stability which is used in dry high-speed cutting [1]. This material can afford high working temperature (800 °C) with low degree of corrosion [2]; this inertia is due to the formation of passive oxide layers on the surface at very high temperatures [3]. ‘Stripping’ or ‘decoating’ TiAlN₂ is an important part of this technology; it is used to recycle unsuccessfully coated parts and more

often for reconditioning used parts after the end of their functional service.

The technology for stripping ceramic coatings is not used just for TiAlN₂, but it is of general use in the coating industry [4]. An effective stripping process must completely remove the coating without causing geometrical changes in the substrate. Since most coatings are designed to be corrosion resistant, it is clear that it is not easy to find a suitable stripping process. A number of methods have been reported [5], mainly based on combinations of oxidizing agents (e.g. H₂O₂) and strong acids (e.g. HF). However, very little is known about the mechanisms of action of these chemicals, nor does there exist systematic comparative data about the effectiveness of the reactants used.

The present work aims at the development and the understanding of new chemical stripping methods with the specific constraint of avoiding the use of fluoridric acid (HF). We used photoelectron spectroscopy (XPS), auger electron spectroscopy (AES) and scanning electron microscopy (SEM) for compositional and morphological investigation and X-ray fluorescence to

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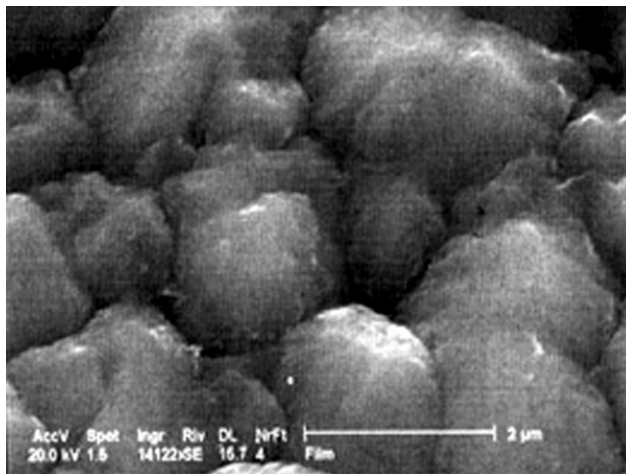


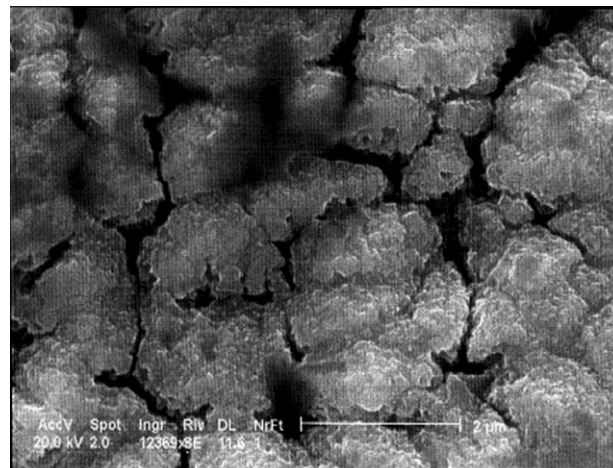
Fig. 1. SEM images of the TiAlN_2 coated sample before stripping (X 14122).

determine the corrosion ratio. We found that it is possible to use a 'surface science' approach to the stripping process and use the data obtained to design chemical processes for a selective stripping of the coating.

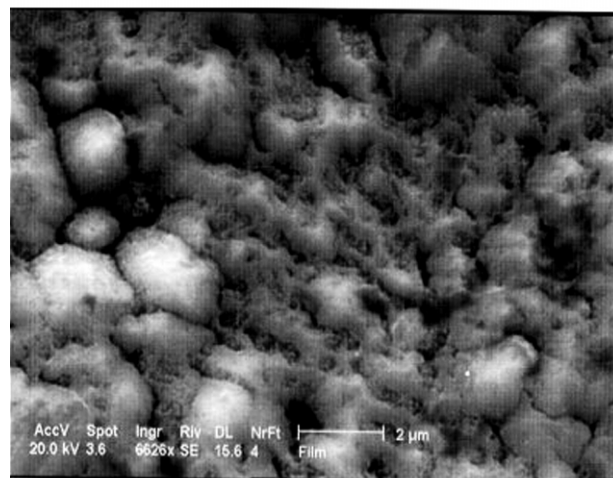
2. Experimental

All the substrates examined in the present study were in hard metal P25, that is in volume percentage WC 52%, TiC 23%, (Ta,Nb)C 10.5% and Co 14% produced with powder sintering methods. These samples were coated with TiAlN_2 by means of reactive magnetron physical vapor deposition (PVD) for a nominal thickness of 4 micron. Actual thickness measurement performed by means of electron microscopy indicated that the average thickness of the samples was of 4.2 ± 0.1 microns. The film composition was monitored by means of X-ray photoelectron spectroscopy (XPS) and by X-ray fluorescence spectroscopy (XRF) and found to correspond to the nominal formula TiAlN_2 within the limits of accuracy of the methods. Before the stripping tests, SEM investigations showed that the TiAlN_2 film was smooth (Fig. 1), with a small porosity which could be originated by grain expulsion from intense internal stress during the coating process. On the uncoated samples we observed a rough surface typical of sintered materials.

Chemical stripping tests were performed by immersing samples in the stripping solutions under continuous magnetic stirring for 2 h, unless otherwise specified. The results were examined first visually, and then by means of electron microscopy (SEM). Information on the surface composition was obtained by surface spectroscopies: X-ray photoelectron spectroscopy (XPS) and auger electron spectroscopy (AES). The oxidation states



(a)



(b)

Fig. 2. SEM images of the samples treated with hydrogen peroxide (a) acid solution (X 12369) (b) Alkaline solution (X 6626).

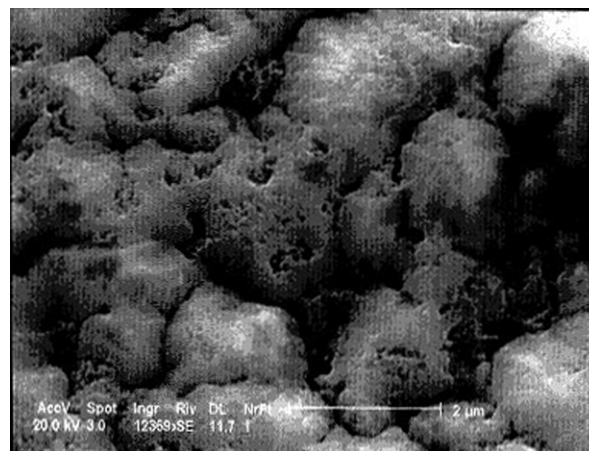


Fig. 3. SEM image of the sample treated with hydrogen peroxide and potassium oxalate in alkaline solution. Pitting corrosion is evident on the grain surface (X 12369).

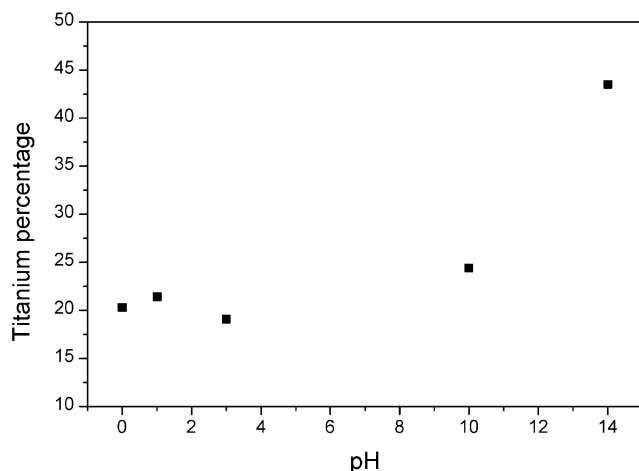


Fig. 4. Surface concentration of titanium determined by XPS spectra in sample treated with hydrogen peroxide and potassium oxalate at different pH. Surface modification is evident the sample treated in alkaline solution.

of the elements were determined in XPS according to the data reported in [6] and in [7] for the specific case of titanium. A direct measurement of the quantity of film present on the surface was obtained from the intensity of the fluorescence signal of aluminum using an XRF spectrometer.

3. Results and discussion

The basic idea of the present work is to combine a selective complexant and a strong oxidizer to form soluble oxides in the reaction environment. Several solutions were tested, and the results reported here are relative to two cases: (i) potassium oxalate and hydrogen peroxide in alkaline conditions; and (ii) potassium permanganate in hot concentrated sulfuric acid. In both

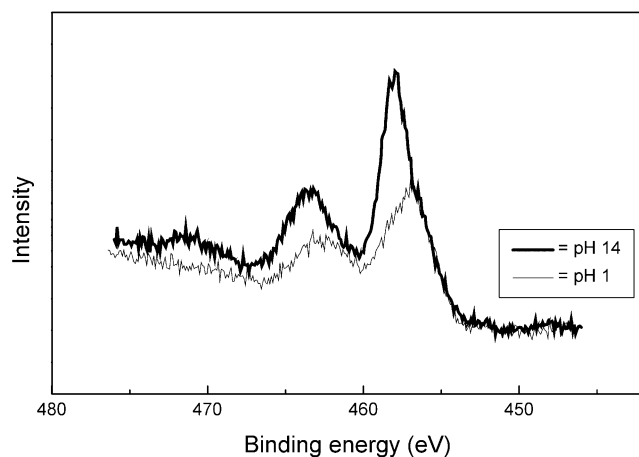


Fig. 5. XPS titanium 3p signal of the samples treated with hydrogen peroxide and potassium oxalate, the change of shape in alkaline solution reveals the formation of titanium dioxide.

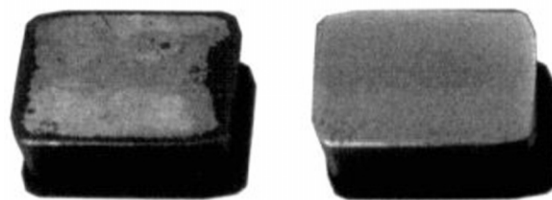


Fig. 6. On the left a sample treated with potassium permanganate in concentrated sulfuric acid shows a black crust that is easily removed by mechanical polishing, on the right the untreated sample.

cases, we tested first the separate reagents in order to determine the ‘best’ conditions of stripping for each, and subsequently the two reagent were combined in a single stripping solution.

3.1. Hydrogen peroxide and oxalate

It is known that hydrogen peroxide alone can remove ceramic films, and in particular nitride films, however, this reactant alone is also known not to be able to remove TiAlN_2 [2]. The oxalate shows an increasing stripping rate in alkaline solution, whereas hydrogen peroxide seems to be more effective at low pH (Fig. 2a) or high pH (Fig. 2b). However, at acidic pH we observed considerable damage to the substrate and the stripping rate remained still too low for industrial applications. For oxalate alone, the XPS data indicate a removal of oxygen and aluminum from the TiAlN_2 film, but that titanium nitride remains present hampering aluminum diffusion and consequent dissolution. For hydrogen peroxide alone also the XPS spectra indicate the disappearance of the oxide.

The system hydrogen peroxide-oxalate seems to be less effective at low pH; the stripping rate is even slower than the peroxide alone. It appears possible that in these

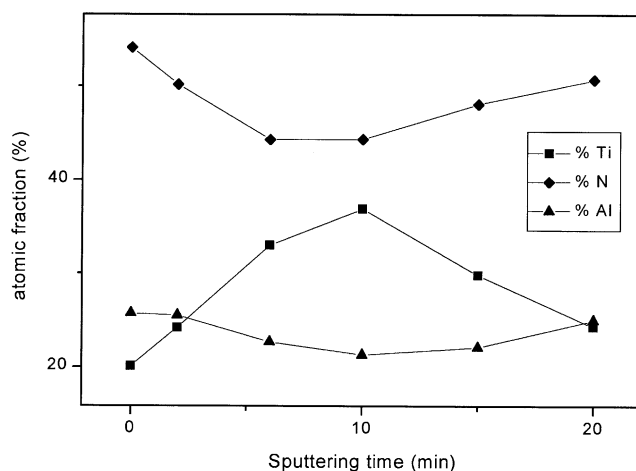


Fig. 7. Atomic fractions obtained by XPS depth profile of the film treated with potassium permanganate in concentrated sulphuric acid.

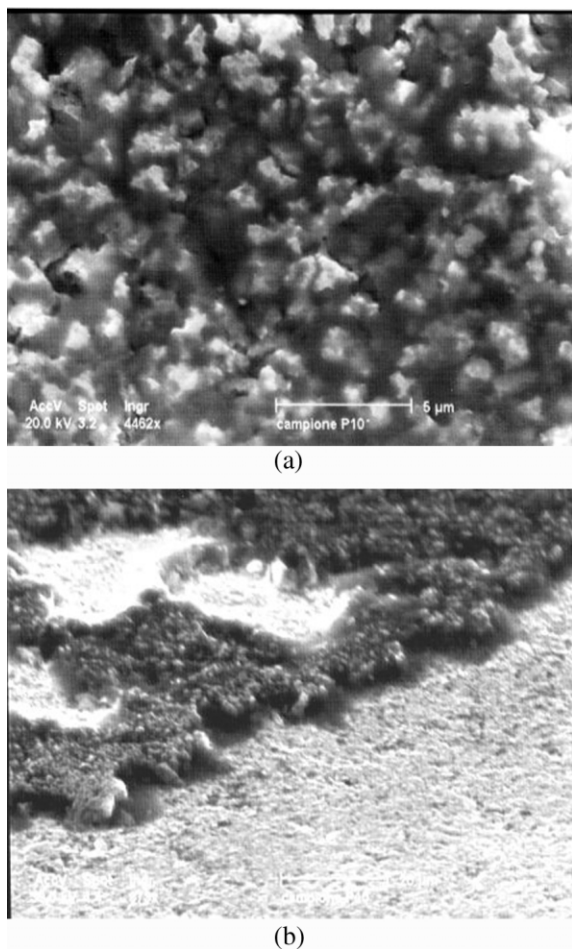


Fig. 8. SEM images of the sample treated with potassium permanganate in concentrated sulfuric acid (a) corroded coated part (X 4462) (b) low magnification image showing the removal of the corroded coating (X 872).

conditions the oxalate is oxidized by the peroxide. In alkaline conditions (pH 14) we found a higher stripping rate. The stripping ratio in these conditions varies from 168 nm/h to 294 nm/h. SEM observations after this treatment (Fig. 3) show a surface with small pits on the grain surface and the absence of intergranular corrosion. This kind of corrosion is totally different from the one observed with hydrogen peroxide solution where the corrosion occurs mostly at grain boundaries. The XPS analysis of the sample treated at pH 14 shows a considerable increase of the titanium concentration (Fig. 4) in comparison to the untreated sample. The shape and binding energy (458 eV) of the Ti 2p XPS signal (Fig. 5) can be interpreted due to titanium dioxide. We also note a decrease in the aluminum and nitrogen concentration. These data indicate a completely different mechanism than that observed for the single reactants. Here, the oxidizer appears to transform both titanium and aluminum into oxides. The presence of the oxalate causes an increase in the dissolution rate of aluminum

but the stripping rate is slowed by the intrinsic poor solubility of the titanium oxide. We also presume that the parallel oxidation of the oxalate can slow down the complexant effect of the oxalate.

3.2. Potassium permanganate in concentrated sulfuric acid

Starting from the observation of the high solubility of titanium in concentrated sulfuric acid [8] we looked for an oxidizer that could transform the inert nitride in oxide. After several tests we found that permanganate is a good oxidizer alone, but that the best results can be obtained by a combination of permanganate and sulfuric acid. In these conditions approximately 2 h are sufficient to transform the shiny-gray TiAlN_2 into a dull black crust (Fig. 6) which can be easily removed with mechanical polishing. The XPS depth profile of the black film revealed the formation of an aluminum enriched surface below the surface contamination. This surface was partially oxidized; in particular, aluminum appears as oxide only. Furthermore, a new component in the XPS nitrogen signal appears. According to literature data [9,10], this component derives from molecular nitrogen entrapped in the oxide layer.

The XPS depth profile (Fig. 7) suggests the formation and the segregation of the two oxides, aluminum segregates at the top and seems to be soluble, below there remains the titanium dioxide layer, containing only traces of aluminum content and eventually at some depth we observe the nominal TiAlN_2 composition, this behavior is comparable with high temperature corrosion, were the two oxides segregates with aluminum on the top layer.

In Fig. 8 we show a SEM micrograph illustrating the corrosion phenomena. The results can be interpreted in terms of weakening of the structure to a critical point where strong internal stresses cause the breaking of the film. The general weakening of the structure was confirmed also by the ease of mechanical removing of the remaining film.

4. Conclusion

Of the two chemical stripping methods tested here, oxalate plus hydrogen peroxide in alkaline conditions was found to be promising but the results are still not satisfactory. A better control and a faster stripping rate are needed. The second chemical solution tested (permanganate in concentrated sulfuric acid) was able to completely remove the coating without apparent damage to the substrate. Further studies are needed for adapting the process to industrial needs, but the present work shows how an approach that considers the atomic level phenomena at the surface can be used for setting up effective decoating process. The use of surface science

methods, such as X-ray photoelectron spectroscopy, appears to be essential for this approach.

Acknowledgments

The authors are grateful to LAFER s.r.l. for supporting the present study.

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